

Shock Tube Study of the Acetylene - Oxygen Reaction

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A number of investigations of the high temperature combustion of acetylene have been reported in recent years. The techniques employed have included probe studies of low pressure flames, spectroscopic studies of atomic flames, and various observations on detonation and shock waves in acetylene - oxygen mixtures. We report here a shock tube study of visible continuum emission, ultraviolet emission and OH absorption in incident shock waves through acetylene - oxygen mixtures.

EXPERIMENTAL

The shock tube was constructed of 2" x 4" aluminum tubing. Observations were made through quartz and lucite windows mounted flush with the tube walls. Velocity measurements were made with a series of flush resistance gauges spaced on either side of the observation station. Continuum emission was observed through the lucite window using an interference filter of about 80 Å bandwidth centered at 4320 Å for wavelength selection and a 1P28 photomultiplier tube for detection. The photomultiplier current pulses were amplified and then converted to logarithmic scale with a high frequency operational amplifier for oscilloscope recording. Ultraviolet emission was observed using a Beckman DU monochromator for wavelength selection and a 1P28 for detection. Absorption studies were made using a light source consisting of a microwave discharge in about 10 mm of argon containing a trace of bismuth vapor. The bismuth resonance line at 3067 Å was isolated with the DU monochromator and used for monitoring OH concentration. Sensitivity of the absorption system was calibrated by observations of OH concentration at chemical equilibrium in shocks through H_2 - O_2 mixtures. The arrangement of the equipment was such that either OH absorption or ultraviolet emission could be observed simultaneously with the continuum emission, and that the origin of the effects observed in the two measuring systems was identical with maximum error of 3 microseconds. The shock tube was readily evacuated to the 10^{-5} mm range and had an outgassing and leak rate of about 2 microns per hour.

Experimental mixtures were prepared in a conventional mercury-pumped vacuum system. The acetylene concentration was about one percent and oxygen concentrations varied from .34 to 7.3 percent, the remainder being argon diluent. Conventional precautions in purification and mixing were observed. Initial pressure in all experiments was 5 mm. No-reaction temperatures computed from shock velocities covered the range 1500 - 2200 °K.

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RESULTS

Both the visible and the ultraviolet radiation appeared as a pulse, following an induction period. The ultraviolet emission, which was observed at 2196 Å, was far weaker than the visible emission, but both had essentially the same pulse shape and appeared simultaneously. Hydroxyl radical concentration rose to values above the detectability threshold, about 10^{-8} moles/liter in these experiments, just the emission pulses were returning to baseline.

Induction times defined by appearance of OH could be plotted as $\log (O_2)_{xt}$ versus $1/T$ as in the hydrogen - oxygen study of Schott and Kinsey or in earlier studies of the acetylene - oxygen reaction by Kistiakowsky and coworkers. The resulting plot showed that the OH induction times were about 2-3 times longer than induction times previously measured for this reaction using observations of onset of density change due to heat release in reaction, vacuum ultraviolet emission or ionization to define the end of the induction periods.

Time constants for the exponential rise in intensity of the continuum emission were obtained from the linear portions of the logarithmically recorded pulses. These, when plotted in the above form, showed no temperature dependence, in contrast to the strong temperature dependence (activation energy about 20 kcal/mole) found by Kistiakowsky and Richards for the time constants of the vacuum ultraviolet exponential rise.

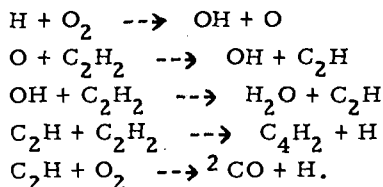
The lack of temperature dependence for the exponential rise constants led to a very strong temperature dependence of the ratio of continuum emission induction time to decadic time constant, which is a measure of the number of decades of concentration through which the emitting species rises as chain branching reactions proceed. At 1800 °K these values scattered around 30, but at 2100 °K they were down to less than 10.

Peak intensity of the continuum pulses was also strongly dependent on temperature. Between about 1600 °K and 2100 °K this was found to increase by about a factor of 10. Emission was strongest in mixtures near stoichiometric.

A search was made for structure in the ultraviolet emission intensity in the region 2000 - 2200 Å. This was done in a series of shocks of nearly constant strength in a lean mixture. The intensity distribution appeared to be uniform.

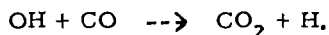
DISCUSSION

Previous shock tube studies on this reaction indicated that the main reaction sequence of the induction period could be understood in terms of the following branching chain sequence:

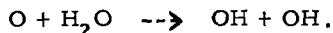


This mechanism was proposed in order to account for the similarity of $\text{H}_2 - \text{O}_2$ and $\text{C}_2\text{H}_2 - \text{O}_2$ induction period behavior and for the appearance of diacetylene in mass spectrometric studies of shocked $\text{C}_2\text{H}_2 - \text{O}_2$ mixtures. Several features of the high temperature reaction are not accounted for, as for example ionization or the appearance of formaldehyde; this provisional mechanism would have these features considered as side reactions not contributing to the main chain. Any side product whose concentration depends on the concentration of main chain species, however, is a satisfactory diagnostic for the progress of the chain reactions. It was proposed by Hand, for example, that the vacuum ultraviolet radiation observed by Kistiakowsky and Richards was due to excited CO produced by reaction of O with CH produced by oxidation of C_2H . The CO emission, therefore, would be an indirect measure of the chain carrier concentrations at any given time. Likewise, the continuum emission observed in this work comes from electronically excited CO_2 , which is produced from reaction of O with CO, and is, therefore, also an indirect measure of chain reaction progress.

Consideration of this reaction sequence shows that OH concentration should become observable when the chain has progressed to the point of giving macroscopic evidence of reaction, i.e. final products or heat evolution. In this work, however, it was found that the OH concentration rises only much later, after most of the final products have been formed. It follows, therefore, that OH is rapidly suppressed against its high rate of production in the chain by other reactions. When the acetylene concentration begins to decrease, this could be



The decay of continuum and ultraviolet radiation appeared to be simultaneous under all conditions, indicating that they probably have a common source. Since one of the reaction partners producing the emitter of the continuum radiation is a stable product, O is the most likely candidate for this role. Its destruction can only be by a final product. A probable pathway is



The lack of temperature dependence found for the exponential growth constant is probably complex in origin. It is likely to be due to a counterbalance of the increasing rate of chain center multiplication, as temperature increases, by increased rate of destruction of those particular species leading to the continuum emission, namely O and CO.

Failure to find the CO 4th positive system in the 2000 - 2200 Å region is probably due to instrumental limitations.

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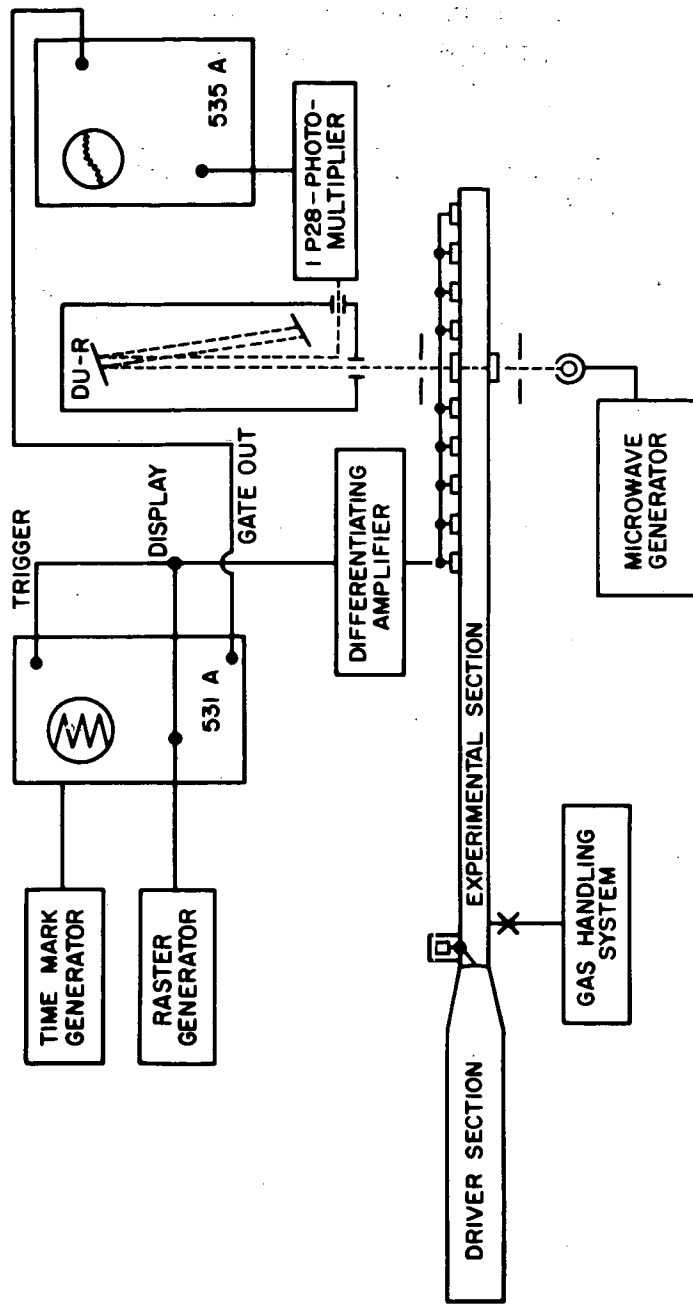


Fig. 1. Block Diagram of Apparatus.

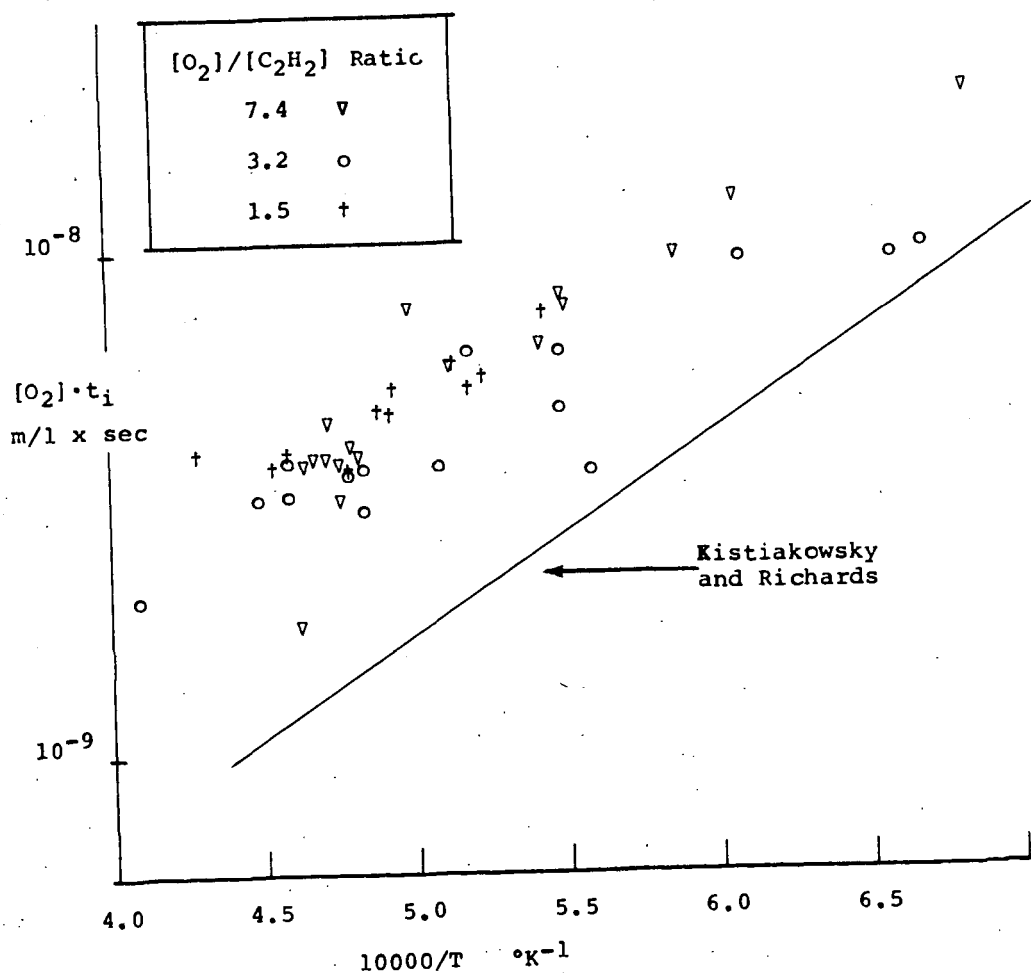


Fig. 2. Induction Times for OH appearance.

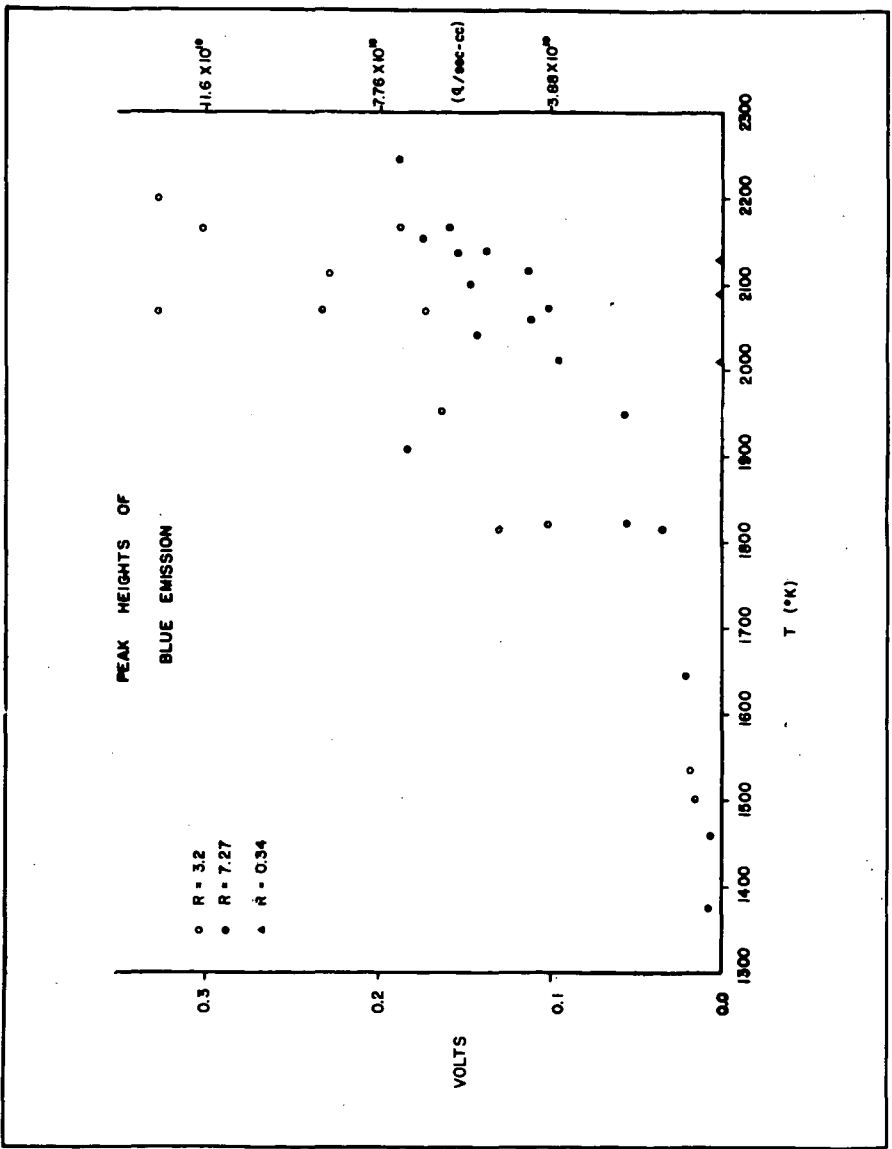


Fig. 3. Peak Intensity of Continuum Emission.